Letter to the Editor

Comments on ''Photocatalytic properties of TiO₂ modified with platinum and silver nanoparticles in the degradation of oxalic acid in aqueous solution'' Langmuir Hinshelwood kinetics—A theoretical study

Recently Iliev et al. [1] published a paper entitled above. No doubt the paper reports an excellent work about the characteristics of the TiO₂ modified with platinum and silver. In addition it is very good to know about the photocatalytic degradation properties of the modified TiO₂ to treat oxalic acid aqueous solution. However I would like to make a note about the Langmuir Hinshelwood kinetics discussed in the above referred paper [1]. The Langmuir Hinshelwood expression that explains the kinetics of heterogeneous catalytic systems is given by:

$$r = \frac{dC}{dt} = \frac{k_r KC}{1 + KC} \tag{1}$$

where r represents the rate of reaction that changes with time.

The term, r in Eq. (1) was represented in terms of initial reaction rate, r_0 as a function of the initial dye concentration, C_0 or in terms of C_e, where C_e is the equilibrium dye concentration in solution after the completion of dark experiments. The initial rate of reaction as a function of C_0 and C_e is given by Eqs. (2) and (3) respectively:

$$r_0 = \frac{k_r KC_0}{1 + KC_0} \tag{2}$$

$$r_0 = \frac{k_r KC_e}{1 + KC_e} \tag{3}$$

The parameters k_r and K which is a function of C_0 or C_e can be predicted by linearizing the Eq. (2) or (3) as follows:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r KC_0} \tag{4}$$

In the paper referred [1], it was reported that for a higher value of $KC_0 \gg 1$, the Langmuir Hinshelwood kinetics as in Eq. (2) was reduced to a Zero order kinetics. However if the LH expression expresses in terms if initial reaction rate, for $KC_0 \gg 1$, the Langmuir Hinshelwood will not reduce to a zero order kinetics. As a case study, the literature data for the photocatalytic degradation of Reactive Orange 16 by TiO2P25

catalyst [2]. Fig. 1 shows the plot of r_0 versus C_e for various KC_e values. Fig. 1 shows the simulated r_0 values using Eq. (2) for experimental values and also for increasing K values. From Fig. 1, it can be observed that for increasing the K values from 2 to 4 times that of the experimental K value, the simulated r_0 values deviated much from the experimental kinetics. This shows the significance of the KC_e in the LH expression as in Eq. (2). This suggests the term KC_e in a Langmuir Hinshelwood kinetics represented in the form of initial reaction rate should not be neglected.

In the case of Eq. (1), the constants k_r and K can be calculated from the integrated expression of Eq. (1). The Eq. (1) can be integrated between the limits: $C = C_0$ at $t = 0$ and $C = C$ at $t = t$. The integrated expression of Eq. (1) is given by:

$$\ln\left(\frac{C_0}{C}\right) + k(C_0 - C) = k_r Kt \tag{5}$$

If the term $KC_e \ll 1$ then Eq. (1) is reduced to:

$$r = k_r KC \tag{6}$$

Integrating Eq. (6) with respect to limits: $C = C_0$ at $t = 0$ and $C = C$ at $t = t$, LH expression reduces to a first order kinetics and is given by:

$$-\ln\left(\frac{C}{C_0}\right) = k_1 t$$

If the term $k_r K \gg 1$, then the denominator of Eq. (1) becomes more significant in predicting the LH kinetics. Thus I would like to point out that for $KC_e \gg 1$, the Eq. (1) cannot be reduced to a zero order kinetics as mentioned in referred paper [1]. If $KC_e \gg 1$, then I suggest to use the Eq. (5) to predict the constants k_r and K in the LH expression.

Thus it is concluded that for $KC_e \gg 1$, if the oxalic acid degradation by TiO₂ modified with platinum and silver if follows a LH kinetics, then the rate kinetics is given by Eq. (1).
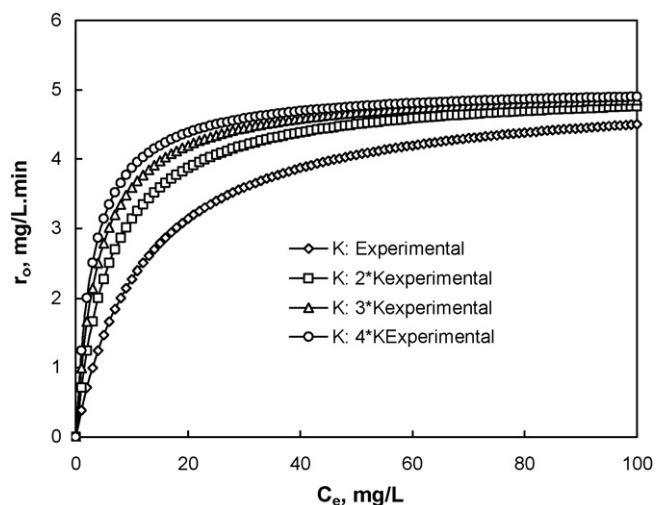
Fig. 1. Plot of r_0 vs. C_e for the photocatalytic degradation of Reactive Orange 16 by TiO$_2$ P25 for different K values.

In addition, for $KC_e \gg 1$, the Langmuir Hinshelwood kinetics cannot be reduced to zero order kinetics. If the oxalic acid degradation by TiO$_2$ modified with platinum and silver catalyst follows zero order kinetics, then the rate expression should be expressed as:

$$-r = -\frac{dC}{dt} = k_0$$

References

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[2] I. Poulios, I. Aetopoulou, Environ. Technol. 20 (1999) 479.

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